Enhancement of luminescence performance from the alteration of stacking pattern of Pt(II) dendrimers

Journal:	*Journal of Materials Chemistry C*
Manuscript ID:	TC-ART-11-2014-002694.R2
Article Type:	Communication
Date Submitted by the Author:	29-Jan-2015
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Enhancement of luminescence performance from the alteration of stacking pattern of Pt(II) dendrimers†

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/C4TC000000

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† Electronic Supplementary Information (ESI) available: experimental details, synthesis and characterization data, crystal structures and packing diagrams, supplementary photophysical spectra and electrochemical characterization and electroluminescent characteristics of OLEDs. CCDC reference numbers 1032774-1032776. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/C4TC000000

Four red emission Pt(II) dendrimers, in which the emitting core and dendron are joined by flexible alkylene chain, have been designed and synthesized. They exhibit nearly identical emissive wavelength both in photoluminescence in solution and electroluminescence. Improved luminescence performance results from the favourable packing pattern compared with their parents. A maximum current efficiency up to 22.11 cd/A, the corresponding power efficiency of 12.29 lm/W and EQE of 11.70%, has been recorded in a doped and solution-processed OLED.

Introduction

Transition-metal Pt(II) complexes are recently gained increasing interest not only for the development of light source and flat panel display as emitters due to their tunable emission and high photoluminescence quantum yield (PLQY, φ_{p}),[1] but also for achieving new function of molecular aggregation in efficient chemosensor and supermolecular electronics from unpredictable packing in the solid state.[2] The latter benefits from their square-planar architecture that allow them to interact facially with one another, in which most of the Pt(II) complex molecules stack as dimer.[1e, 3] In contrast, as an emitter, aggregation will lead to the generation of broad features, such as red-shifted emission from excimer and self-quenching, which severely impair their luminescence efficiency and stability.[4] In this regard, Pt(II) complexes with dendrimeric structure are found to display an intriguing character of encapsulating and isolating the emitting core that can be harnessed for controlling intermolecular aggregation.[5] However, it remains a challenge to completely eliminate intermolecular interaction because the backbones of ligands in the reported dendrimeric Pt(II) complexes are always comprised of aromatic groups, which can minimize non-radiative decay. Moreover, in order to keep chemical structure more stable, the intermolecular interaction in the Pt(II) complexes seems inevitable due to their 16e unsaturated coordination and open square-planar configuration.[6]

In our previous work,[7] the dendrimeric Pt(II) complexes distinctly exhibit the improved luminescence properties relative to their parents due to the introduction of bulky group and carbazolyl dendron. However, the rigid linkage of phenyl ring fixes the orientation of the dendron, which still retains the enough space for the intermolecular interaction in addition to a little influence on the emission wavelength due to its donating character. These Pt(II) dendrimers, especially with smaller generation and less dendron number, are still prone to stacking as dimer at high concentration or in the solid state.

Recently, non-conjugated alkyl and oligo(ethylene glycol) chains have been incorporated in molecular skeleton of organic semiconductor material, which lead to distinct optoelectronic property and device performance owing to the ingenious variation in molecular packing.[8] Naota and co-workers also demonstrated that the Pt(II) complexes with the longer alkylene chain are prone to form more compact packing structures, and achieve precise OFF-ON control of emission.[9] These works indicated that the linkage of non-conjugated alkyl chain between the dendron and the emitting center in Pt(II) dendrimers might provide an approach to adjust intermolecular interaction. On the other hand, the linkage mode maybe less affect the photophysical property of Pt(II) dendrimer in OLED device due to its non-conjugated nature.

In this work, we designed and synthesized four heteroleptic Pt(II) dendrimers, in which the emitting core (PPQ)Pt(acac/dpm) (PPQ = 2,4-diphenylquinoline, acac = acetylacetone, dpm = dipivaloylmethane) and carbazole-based dendron are joined together using a flexible *n*-butylene chain, as shown in Scheme 1, and two rigid dendrimers of **D1-1** and **D1-2** with *p*-phenylene linkage for comparison. The flexible connection never affects photoluminescence (PL) property of the emitting core, but alters the molecular packing pattern. The unexpected packing not only plays a shielding effect but also generates a host material function. Correspondingly, the eletroluminescent (EL) performance is improved effectively in the doped devices relative to the rigid Pt(II) dendrimers.

Scheme 1 here

Results and discussion

The Pt(II) dendrimers were prepared by a modified two-step procedure involving the reactions of the proligand with K_2PtCl_4 in a mixed solvent to form Pt(II) intermediates, and the intermediates with ancillary ligands in the presence of base to afford the pure products in moderate yield (24-45%) after column chromatography (see ESI for synthesis).[1e, 7, 10] These complexes were characterized by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry and elemental analyses. TGA showed they have good thermal stabilities with decomposition temperatures above 285 ºC (Table 1).

Single crystals **D1-2** and **C4-D1-2** suitable for the X-ray diffraction were obtained by slow evaporation of a DCM/MeOH solvent. The molecular structures of **D1-2** and **C4-D1-2** are shown in Figure 1 and S1. The selected bond distances and angles are summarized in Table S3. Despite an addition of a flexible butylene group in **C4-D1-2**, the bond lengths and angles around the Pt(II) atom are similar to those in **D1-2** and the parent complex **(PPQ)Pt(acac)** (Figure S1), and fall within normal ranges.[1e, 3e] The **(PPQ)Pt(dpm)** motif in **D1-2** and **C4-D1-2** is always a slightly distorted square-planar geometry with the dihedral angles of 4.14° for **D1-2** and 4.44° for **C4-D1-2** between the coordination planes PtC1N1 and PtO1O2 (Figure S3). The deformation is from the repulsion between the H atoms of PPQ and the bulky *t*-butyl groups of dpm (the corresponding torsion angles are listed in Table S3).[11] Consequently, a significant impact on luminescent efficiency has been observed upon the coordination environment of the emitting core, as discussed in electroluminescence section.

Figure 1 here

The absorption (Figure S4, ESI) and luminescence spectra (Figure 2) of the Pt(II) dendrimers were measured in DCM solution at the concentration of 10^{-5} M at room temperature. The corresponding data were summarized in Table 1. All Pt(II) dendrimers exhibit intense absorption peaks at energy below 360 nm, which are attributable to the primarily spin-allowed ligand-centered (LC) transitions compared with the absorption spectra of the free ligands (Figure S5). The lowest energy absorption bands in the region of 409-415 nm are assigned to $d_{\pi}(Pt) \rightarrow \pi^*(L)$ metal-to-ligand charge transfer (MLCT) mixed with triplet LC transitions. These bands have a higher molar absorption coefficient (by a factor of ca. 4, Table 1) relative to the Pt(II) analogues reported in literatures (factor ≈ 3) [1c, 12], which means a strong mixing of MLCT character into the lowest exited state and make these Pt(II) dendrimers highly desirable as phosphorescent emitters for OLEDs.

Figure 2 and Table 1 here

The flexibly-connected Pt(II) dendrimers in DCM solution show board and bright red phosphorescence at room temperature (Figure 2, top) with identical emission maxima at 608 nm to those of their parents **(PPQ)Pt(acac)** and **(PPQ)Pt(dpm)** (Figure S6), suggesting that these Pt(II) dendrimers and their parents have same orbital parentage from the lowest emissive triplet states to the ground state.[11] Moreover, the emissions originate from the absorption bands around 345 and 409 nm according to the absorption and PL excitation spectra (Figure S7, top).[7] In contrast, the PL spectra of the rigidly-connected **D1-1** and **D1-2** display a red shift emission of 5-6 nm (10^{-5} M, Table 1), which should be caused by the intermolecular interaction according to our previously study and their doped EL spectra (Figure 3).[7, 13] These results indicate that the flexible connection has less influence on the electronic structure of the Pt(II) dendrimers. In neat films, these complexes exhibit a different extent of red-shifted emission. As depicted in Figure 2 (bottom), on going from **D1-1** to **C4-D1-1**, 20 and 16 nm red shifts are observed relative to **(PPQ)Pt(acac)** in solution, indicating that aggregate still exists at high concentration. With increase of the generation of dendron, **C4-D2-1** only gives rise to 2 nm red shift under the same condition, suggesting that the intermolecular interaction is nearly completely eliminated. It can be seen that introduction of the flexible connection group is helpful for the improvement of encapsulation and isolation capability in the square-planar Pt(II) complexes compared with the rigidly-connected analogue (6-7 nm red shift).[7, 10] For the Pt(II) dendrimers with dpm as ancillary ligand, their PL spectra blue-shift 7~25 nm compared with those of acac analogues in the neat film. The blue-shifted emission was also observed for **C4-D1-2** and **C4-D2-2** when the emission spectra were collected from solution to neat films. It should be ascribed to the lower highest occupied molecular orbital (HOMO) energy (Figure S8) imparted by the distorted square planar geometry, although the bulky dpm ligand can effectively inhibit the intermolecular interaction.

The lifetimes of Pt(II) dendrimers are within reasonable scope of emission decay time (1.76~5.18 μs, Table 1) in degassed toluene solution and neat film, which make them avoid effectively saturation and/or T-T annihilation.[14] With **D1-1** and **D1-2** as reference, the PLQYs of **C4-D1-1**, **C4-D1-2**, **C4-D2-1** and **C4-D2-2** show a little enhancement after incorporating flexible butylene group and higher generation dendron in optically dilute solution. The radiative decay rate constants (k_r), estimated from the PLQY and lifetime data, are similar by a factor of 4 for these Pt(II) dendrimers, but lower than those of red Pt(II) complexes with diphenylpyrazine ligand.[11] This can be attributed that the higher Huang-Rhys factor (S_M) make the radiative transition become more complicated in the diphenylquinoline-based Pt(II) complexes according to their board and no vibronically featured PL spectra.[12, 15] On the other hand, the less resolved emission spectra mean more deactivation channels of the emissive excited state, which lead to an increase of the non-radiative decay rate.[16] The larger non-radiative decay rate constants (k_{nr}) listed in Table 1 (factor ≈ 5) support our speculation. However, the k_{nr} values show a downward trend on going from **D1**, **C4-D1** to **C4-D2**, indicating that incorporating flexible connection group and higher generation dendron could effectively protect the emitting core from the occurrence of some unnecessary quenching processes, such as T-T annihilation.

OLED devices employing these Pt(II) dendrimers as emitters were fabricated in the following device structure: ITO/PEDOT:PSS (50 nm)/4% Pt(II) dendrimer:CBP (30 nm)/TPCz (60 nm)/LiF (1 nm)/Al (100 nm) (see ESI, Figure S10). The most efficient devices were achieved with doping concentration of 4% by weight in emitting layer. The corresponding EL spectra and performance characteristics for each device are displayed in Figure 3 and 4. A summary of device performance at the brightness of maxima is tabulated in Table 2. As shown in Figure 3, all devices give nearly identical board red electroluminescence with a peak wavelength of 608 nm and Commission Internationale de L'Eclairage (CIE) coordinates around (0.56, 0.42). Unlike other Pt(II) complexes with C^N bidentate ligand, they do not show any obvious shoulder band closely related to aggregates.[3e, 17] The EL spectra largely resemble the PL spectra of their parents in solution, revealing that any unfavourable intermolecular interactions have been excluded at doped device condition.

Figure 3 and 4, Table 2 here

The turn-on voltages in the devices range from 4.5 to 5.2 V, and are relatively low among solution-processed OLEDs based on Pt(II) complexes.[1d] Although these Pt(II) dendrimers have moderate PLQYs in solution, the OLEDs give satisfactory EL efficiencies. Dendrimer **C4-D1-1** displays the maximum current efficiency (CE) of 20.72 cd/A, power efficiency (PE) of 10.80 lm/W and EQE of 11.00%, which are obviously higher than the rigidly-connected dendrimer **D1-1** (15.45 cd/A, 8.30 lm/W and 9.04%). The maximum CE of **C4-D2-1** reaches up to 22.11 cd/A with PE 12.29 lm/W and EQE 11.70%, and only decreases to 20.05 cd/A (PE 9.50 lm/W and EQE 10.36%) at 100 cd/m^2, suggesting that the self-quenching effect is depressed with increasing the size of the dendron. A similar upward trend is observed for the corresponding Pt(II) dendrimers with dpm ancillary ligand. For example, the maximum EQEs are 10.98, 11.04 and 11.60% for the devices of **D1-2**, **C4-D1-2** and **C4-D2-2**, respectively. To our knowledge, these efficiency data are comparable to those of solution-processed OLEDs incorporating green Pt(II) emitters and superior to the red phosphorescent Pt(II)-complex-based OLEDs reported previously.[1d, 3e, 18] However, no obviously enhanced efficiency for the devices of **C4-D1-2** and **C4-D2-2** was observed in comparison with the corresponding **C4-D1-1** and **C4-D2-1** under the same condition, which is predictable because the emitting core in the formers has a more distorted square planar geometry (Figure S3).[3e]

As shown in Figure 5a, two adjacent **D1-2** molecules form a stacked dimer, in which there exist the *d*-*π* and *π*-*π* intermolecular interactions between the emitting core and 4-phenyl ring with a distance of 3.611 Å, and two quinoline ring planes with a separation of 4.040 Å, respectively. The *d*-*π* and *π*-*π* interactions would result in the emissive defects, which had been well documented in the literatures.[3e, 19] In contrast, for the flexibly-connected **C4-D1-2**, the *π*-*π* intermolecular interactions are from quinoline and carbazole units with the nearest distances of 3.722 and 3.748 Å rather than two emitting cores (Figure 5b). These special *π*-*π* interactions that are not completely from the emitting core are beneficial for improving emission performance. Because in the case the carbazole unit not only acts as the peripheral substituent to encapsulate and isolate the emitting core, but also restrict the energy transfer and electron exchange between it and the emitting core due to its high triplet energy (3.0 eV).[20] Thus, the flexibly-connected Pt(II) dendrimers have better "self-host" feature than the rigid counterparts due to the alteration of stacking pattern, reflecting in the obviously increased EL efficiencies.

Figure 5 here

Conclusions

A novel type of the flexibly-connected Pt(II) dendrimers has been synthesized and characterized. Their OLED devices exhibit more efficient phosphorescence performance compared with the rigid analogues. The maximum CE, PE and EQE up to 22.11 cd/A, 12.29 lm/W and 11.70% were achieved in solution-processed OLED using the flexibly-connected dendrimer **C4-D2-1** as emitter. The improvement should be attributed to the alteration of the molecule stacking pattern that was confirmed by the solid state structure. The replacement of phenyl ring by alkylene group not only has less influence on the property of the emitting core but also changes the orientation of the dendron due to the non-aromatic characteristic of the flexible chain. More important, the change results in a favourable intermolecular interaction between the emitting core and the peripheral substituents with a host material function. Therefore, the flexible linkage might be a novel strategy to develop the efficient phosphorescent Pt(II) materials, although more study needs to be carried out in order to precisely control the positive intermolecular interaction in addition to maintaining effective shielding effect on the emitting core.

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (No. 21204083, 21404101 and 51073152).

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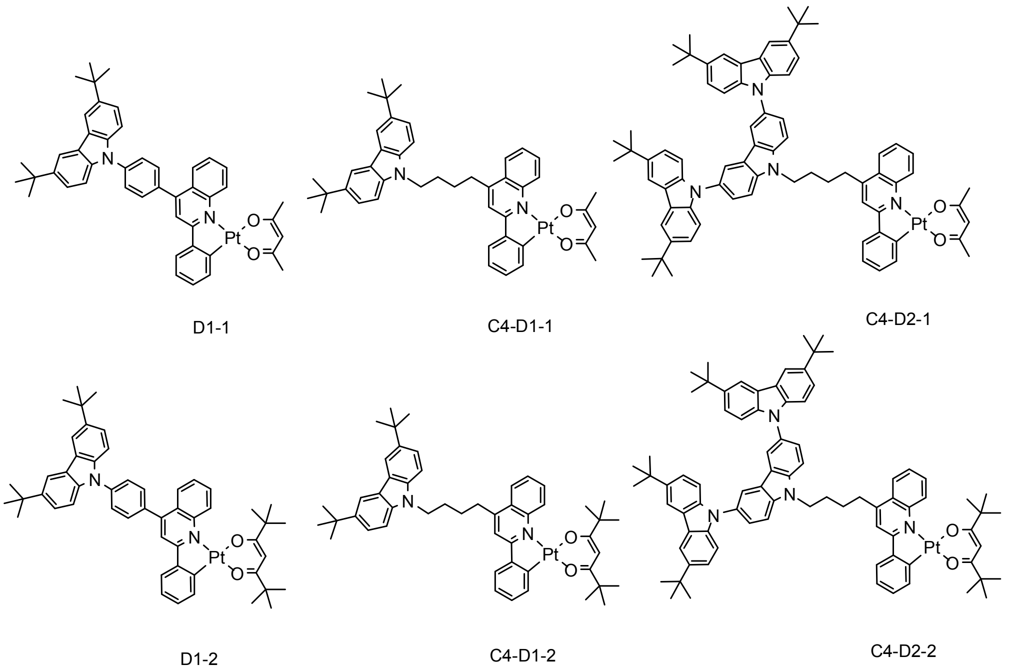

Scheme 1 Molecular structures of the Pt(II) dendrimers.

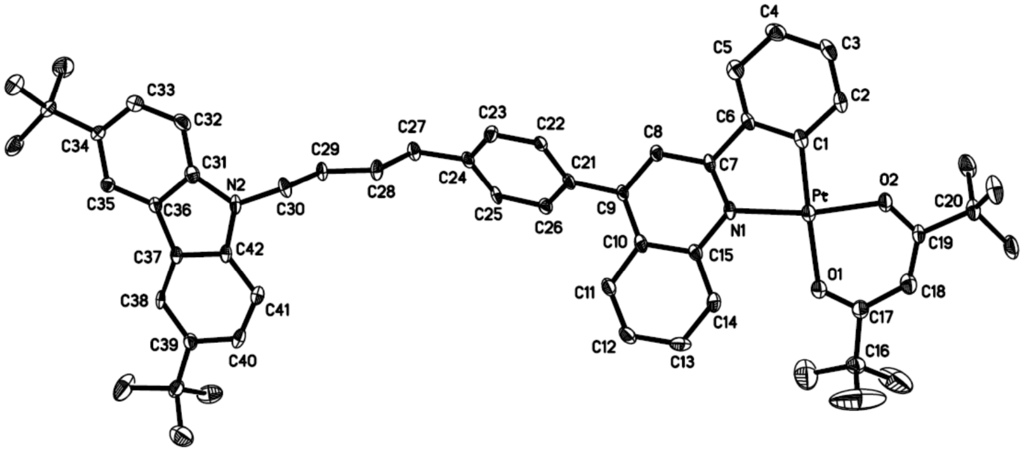

Figure 1 Perspective view of complex **C4-D1-2** with thermal ellipsoids shown at the 30% probability level limit (hydrogen atoms and solvent have been omitted for clarity).

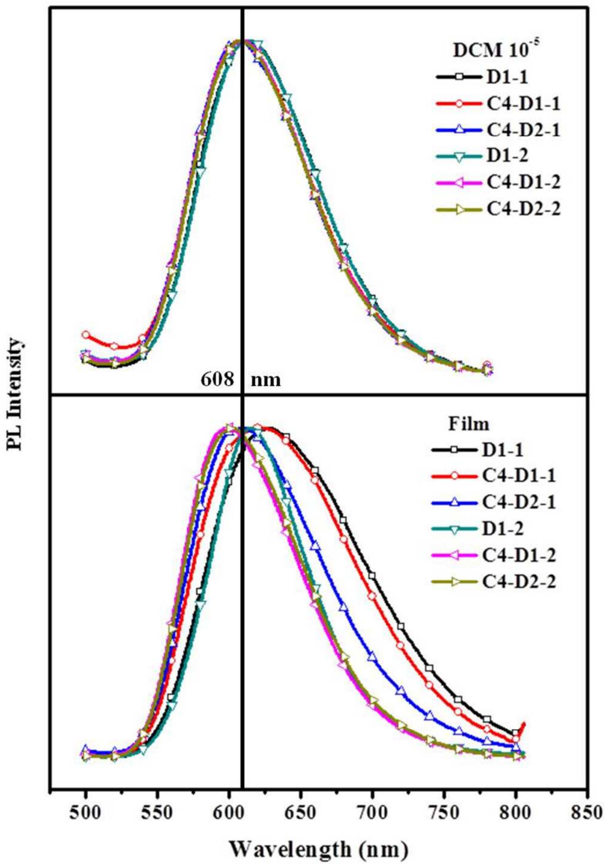

Figure 2 PL spectra of the Pt(II) dendrimers in DCM solution (10^{-5} M) and neat film.

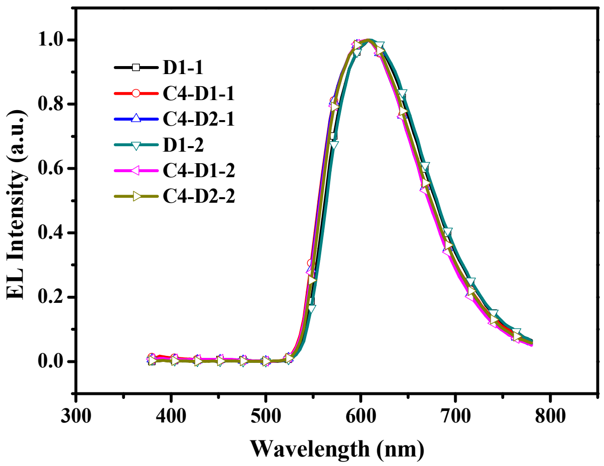

Figure 3 EL spectra at the diving voltage of 8 V for the Pt(II) dendrimers.

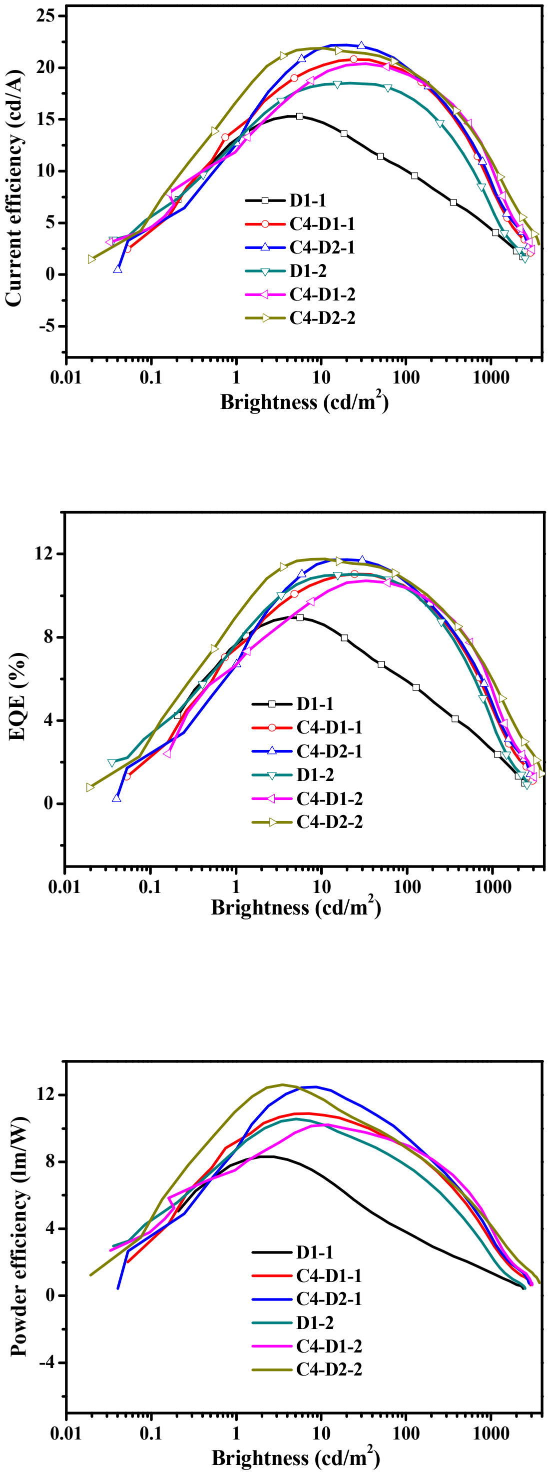

Figure 4 Brightness-current/external quantum/powder efficiency characteristics of the Pt(II) dendrimers.

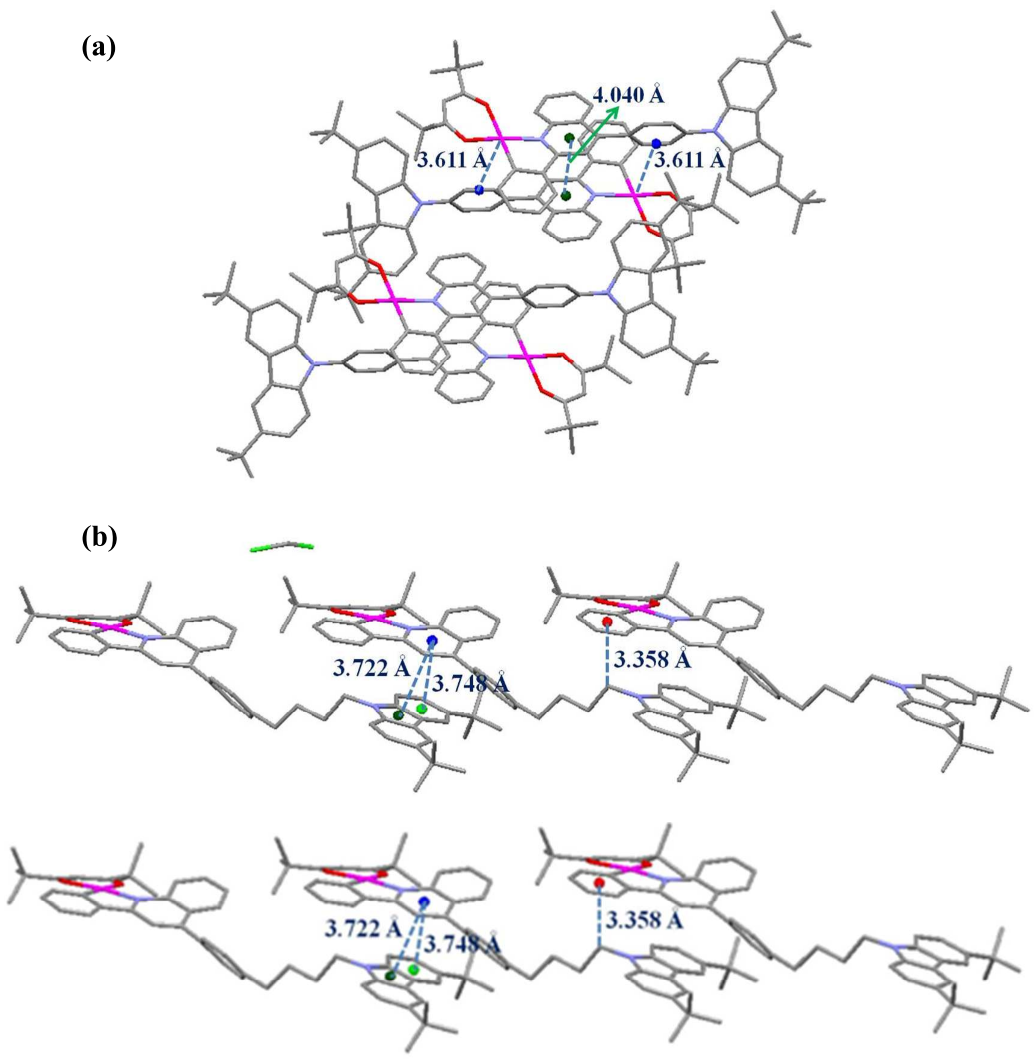

Figure 5. Crystal packing diagram of dendrimers **D1-2** (a) and **C4-D1-2** (b) (hydrogen atoms have been omitted for clarity).

Table 1 Photoluminescence data of the Pt(II) dendrimers at room temperature.

Complexes	λ_{abs}[a] **(logε) (nm)**	λ_{em} **(nm)**[a] **[τ (μs)]**[b]	λ_{em} **(nm)**[c] **[τ (μs)]**[c, d]	φ_P[b]	k_r[e] **($\times 10^4$ s^{-1})**	k_{nr}[e] **($\times 10^4$ s^{-1})**	T_d[f] **(°C)**
D1-1	213 (4.9), 220 (4.9), 231 (4.8), 245 (4.9), 296 (4.7), 332 (4.2), 345 (4.2), 357 (4.2), 413 (4.2)	613 [2.82]	628 [2.10]	0.08	2.84	32.62	309
C4-D1-1	228 (5.0), 232 (5.0), 241 (4.9), 249 (4.8), 262 (4.8), 269 (4.7), 288 (4.7), 299 (4.7), 325 (4.4), 354 (4.1), 410 (3.9)	608 [4.30]	624 [1.76]	0.09	2.09	20.93	293
C4-D2-1	220 (5.0), 241 (5.2), 266 (4.9), 289 (4.9), 297 (4.9), 336 (4.3), 351 (4.3), 409 (4.0)	608 [4.61]	610 [3.50]	0.11	2.39	19.31	301
D1-2	220 (4.7), 232 (4.8), 245 (4.9), 297 (4.7), 332 (4.2), 345 (4.2), 357 (4.2), 414 (4.2)	614 [3.12]	615 [4.02]	0.07	2.24	29.81	355
C4-D1-2	214 (4.6), 232 (4.8), 241 (4.8), 250 (4.7), 263 (4.6), 299 (4.7), 324 (4.1), 339 (4.1), 354 (4.1), 414 (3.9)	610 [3.29]	599 [4.94]	0.10	3.04	27.36	285
C4-D2-2	220 (5.0), 233 (5.2), 240 (5.2), 266 (4.9), 288 (4.9), 297 (5.0), 336 (4.3), 352 (4.3), 415 (4.0)	608 [5.18]	603 [3.93]	0.13	2.51	16.80	313

[a] Measured in DCM solution (10^{-5} M). [b] Measured in degassed toluene solution, and (ppy)Pt(acac) ($\varphi_P = 0.15$) is used as the reference. [c] Measured in neat films. [d] Argon atmosphere. [e] The k_r and k_{nr} values are calculated by followed equations on the assumption that Φ_{ISC} is 1.0. $\Phi_P = \Phi_{ISC}\{k_r/(k_r + k_{nr})\}$; $\tau = (k_r + k_{nr})^{-1}$. [f] 5% mass fraction.

Table 2 Electroluminescence data of the Pt(II) dendrimers at room temperature.

Complexes	**V_{on} (V)**	**Brightness ($cd \cdot m^{-2}$)**	**η_c ($cd \cdot A^{-1}$)**		**η_p ($lm \cdot W^{-1}$)**		**EQE (%)**		**λ_{em} (nm)**	**CIE at 8 V (x, y)**
			max	**@100 $cd \cdot m^{-2}$**	**max**	**@100 $cd \cdot m^{-2}$**	**max**	**@100 $cd \cdot m^{-2}$**		
D1-1	5.2	2647	15.45	10.08	8.30	3.80	9.04	5.91	608	(0.58,0.41)
C4-D1-1	4.8	2924	20.72	19.58	10.80	8.81	11.00	10.36	608	(0.56,0.42)
C4-D2-1	4.5	2820	22.11	20.05	12.29	9.50	11.70	10.36	608	(0.56,0.42)
D1-2	4.6	2519	18.43	17.32	10.30	7.73	10.98	10.34	608	(0.59,0.41)
C4-D1-2	4.9	3068	20.94	19.39	9.91	9.02	11.04	10.61	608	(0.56,0.42)
C4-D2-2	4.7	3750	21.59	19.95	12.55	8.82	11.60	10.69	608	(0.57,0.42)

V_{on}, turn on voltage. η_c, luminous efficiency. η_p, power efficiency. EQE, external quantum efficiency. CIE, commission interbationale de l'Eclairage.

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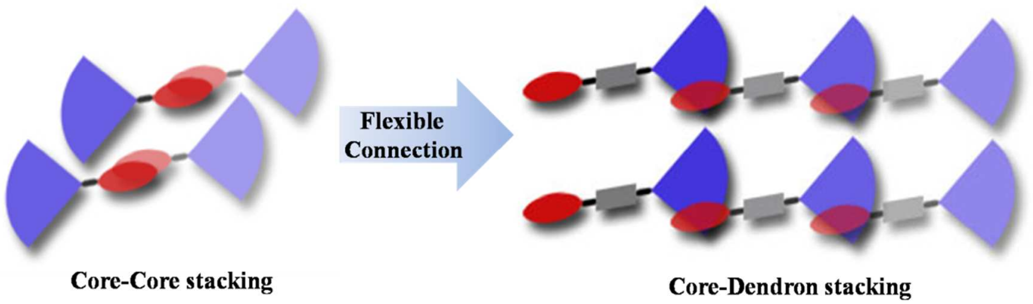

The favourable packing pattern is from the alteration of connection group between the emitting core and dendron in the Pt(II) dendrimers.